yethyl methacrylate ("BTDA-HEMA"), and (3) 4-methacryloxyethyltrimellitic anhydride ("4-META").

Alternatively, but less preferred, in the case of vital dentin, the surface to be treated may be contacted with a strongly acid solution, but still containing NPG, NTG-GMA, NPG-GMA, and/or other amino acids; followed by contacting with PMDM, BTDA-HEMA and/or 4-META monomer solution. Also, an acidic solution and the NPG or other amino acid solution can be applied separately, one after the other (instead of as a combined solution), before the PMDM or other monomer is applied. The components for practicing the method of the invention may be conveniently made available in the form of a kit or article of manufacture.

In one embodiment of the invention, it has been discovered recently that the presence of nitric acid in the first aqueous treatment solution in the absence of ferric oxalate results in high bond strengths for the bonding of composite materials and resins to dentin and enamel. An aqueous solution of nitric acid is contacted with the surface of the dentin or enamel, after which the surface is washed and dried. Subsequent to washing and drying the surface, a solution of NPG, NTG-GMA and/or NPG-GMA in acetone is contacted with the surface. Any excess of the NPG, NTG-GMA, or NPG-GMA is removed by the application of clean acetone which is then removed before it evaporates, and the surface is dried. An acetone solution of PMDM, BTDA-HEMA and/or 4-META is then applied. Finally, the surface of the dentin or enamel is dried. The surface is then ready for application of a composite or dental resin which, upon hardening, will adhere to the substrate surface.

In a preferred embodiment of the invention, it has been discovered more recently that NPG and/or other amino acids can be combined in an aqueous nitric acid solution, and this one solution applied in place of the first and second treatment solutions of the above method. An acetone solution of PMDM, BTDA-HEMA and/or 4-META is then applied. One advantage of NPG is that it is widely commercially available. It is used commercially in the preparation of synthetic indigo blue, which is employed for dyeing denims. Another advantage of NPG is that it is not vulnerable to premature polymerization during synthesis or storage, either pure or in solutions, because it does not contain monomeric moieties (methacrylate groups). The acidic NPG solution is best stored in and dispensed from anaerobic containers.

A particularly preferred method of the invention is accomplished by treating the surface of the dentin, enamel or other substrate containing or capble of binding metallic ions with a solution which contains (1) at least one salt of a polyvalent cation which can bind to substrate surface sites; (2) a compound which contains at least one acid group and preferably two or more acidic groups; (3) a strong acid; and (4) at least one surface-active compound selected from the group consisting of NPG, alpha or beta amino acids, and other compounds each of which contain at least one of each of the following groups: carboxyl and amino. The surface-active compound may be a surface-active comonomer which contains a moiety capable of free radical polymerization as well as the carboxyl and amino groups. The resultant substrate surface is then treated with a solution which contains at least one compound selected from the group consisting of (1) PMDM, (2) BTDA-HEMA, (3) 4-META, (4) other compounds containing at least one group or moiety capable of free radical polymerization, and at least one aromatic ring or moiety containing electron-withdrawing substituents which do not interfere with free radical polymerization, and which compound preferably also contains one or more free carboxyl groups, or anhydride groups which can form free carboxyl groups upon hydrolysis, and (5) camphoroquinone.

DESCRIPTION OF PREFERRED EMBODIMENTS

The Most Highly Preferred Embodiments of the Invention as Simplified

This aspect of the invention comprises improved materials and simplified methods for providing strong adhesion of composite materials and resins to dentin and enamel. The invention also comprises the resultant products. The terms "composite material" and "composite resin" are used herein to refer to materials which contain fillers and which can polymerize or harden by a free radical mechanism. "Resins" refers to monomers (or their polymers) without significant filler content. Typical examples include methacrylates, acrylates, and polyesters.

The most preferred inventive method for preparing the substrate surface for adhesion of composite materials and resins comprises contacting the surface with two solutions, one after the other. The first solution comprises (1) at least one or more polyvalent cations (preferably Al^{3+}) which can form relatively water-insoluble precipitates with phosphate ions; (2) a compound with at least one carboxyl group and preferably two or more carboxyl groups which can form relatively insoluble precipitates with calcium and other polyvalent cations at pH values above that of the acidic treatment solution; (3) a strong acid; and (4) an amino acid.

The most preferred polyvalent cation was discovered to be the trivalent aluminum ion in dental applications where aesthetics is important in view of the possibility that ferric ion can lead to staining by reduction to ferrous ion in the presence of sulfide. The latter can be generated by the metabolic activity of anaerobic microorganisms. Sulfide does not form black complexes with aluminum ions under conditions of interest.

It was also discovered empirically that aluminum oxalate is soluble in water when formulated with the other ingredients of the present invention. Although literature references list aluminum oxalate as insoluble in water, it was discovered that aluminum oxalate is soluble in water, depending upon stoichiometry and pH. Aluminum oxalate does not precipitate from the aqueous solution of the present invention. Aluminum ions can be expected to form insoluble, metastable, microporous, quasi-amorphous precipitates of phosphate as the aqueous solution reacts with dentin and enamel surfaces. Aluminum ions can also be expected to strengthen the altered substrate surface structures by crosslinking and reinforcing the collagenous component of dentin surface reacted upon by the first aqueous solution of the present invention. In applications where color stability and aesthetics are not deciding factors, aluminum ions, ferric ions, and other polyvalent cations can be used separately or in combinations in the first aqueous solution of the present invention. An important function of the precipitation of one or more polyvalent cations with phosphate ions and/or collagenous and/or organic components is thought to be the occluding or obturating of dentinal tubules in vital dentin so as to